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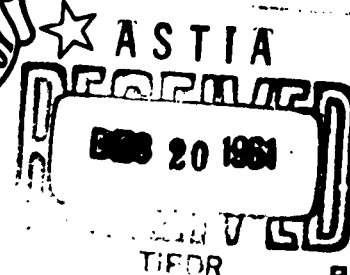
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SCHOOL OF ENGINEERING

THESIS

WRIGHT-PATTERSON AIR FORCE BASE, OHIO

**EFFECTS OF FINE REFRACTORY DISPERSION ON THE COMPRESSIVE
STRENGTH OF A GLASSY-BONDED CERAMIC MATERIAL**

THESIS

**Presented to the Faculty of the School of Engineering of
the Institute of Technology
Air University
in Partial Fulfillment of the
Requirements for the Degree of
Master of Science**

by

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August 1961

Preface

The experiments reported in this thesis were made to determine the effects of a submicron refractory precipitate on the compressive strength of a glassy-bonded ceramic material. A Silicon-Boron-Oxygen system, a new ceramic material currently being studied by the United States Air Force for high temperature application, was used as the model for this study.

This investigation was sponsored by the Metallurgy Research Branch of the Aeronautical Research Laboratory at Wright-Patterson Air Force Base, Ohio. The facilities of the laboratory and the Institute of Technology were used in this study.

I would like to express my appreciation and indebtedness to Lt. Moses P. Davis and Captain Harry F. Rizzo for their invaluable assistance and guidance in this investigation. I would like to thank all the personnel of the Metallurgy Research Branch for their considerate assistance and encouragement. Grateful acknowledgment is expressed to Dr. Paul Rider for guidance in statistical analysis, S/Sgt A. J. Stec for assistance with metallographic studies, Mr. H. R. Kremer for photography, and to Merrill Corkum for the painstaking job of typing this thesis. I would like to express my appreciation to Professor P. H. Keister and Captain E. J. Myers, Institute of Technology thesis committee members, for their interest and suggestions.

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Abstract

The effects of a submicron precipitate, B_7O , on the compressive strength of a Silicon-Boron-Oxygen ceramic material were determined. The quantity of the submicron precipitate was increased in increments of 25 percent by substitution of amorphous boron for crystalline boron in a silicon + 35 weight percent boron model ceramic system. The average compressive strength increased from 195,740 psi for 100% crystalline boron to 234,240 psi for 100% amorphous boron. The increase in the compressive strength was attributed to a change of the internal stresses and impediment of crack propagation resulting from the introduction of the submicron precipitate, B_7O , into the borosilicate matrix.

EFFECTS OF FINE REFRACTORY DISPERSION ON THE COMPRESSIVE
STRENGTH OF A GLASSY-BONDED CERAMIC MATERIAL

I. Introduction

The purpose of this investigation is to determine the effects of a submicron precipitate on the compressive strength of a glassy-bonded ceramic. A Silicon-Boron-Oxygen ceramic is used as the model for this investigation.

The increasing need for high-temperature materials for various Air Force applications has initiated extensive research on the mechanical properties of ceramics. A few metal alloys have satisfactory strength at 1500 °F, but above this temperature their strengths generally decrease rapidly. Above this temperature the carbides and oxides of metals have an inherent advantage over metallic alloys. Generally the melting points are higher, the densities are lower, and the strength of the material is retained. Designers have been considering ceramic materials because of their favorable properties at high operating temperatures.

A new ceramic material consisting of sintered Silicon-Boron-Oxygen was investigated by Rizzo, Weber, and Schwartz (Ref: 11: 497-501) and appeared to have promising compressive strength and high-temperature properties. This ceramic material is composed of free silicon, a boride phase, and an oxide phase dispersed in a borosilicate glass. This study is intended to supplement the research being conducted by the Aeronautical Research Laboratory on the Silicon-Boron-Oxygen system.

This investigation is intended to provide basic knowledge on the effects of a submicron precipitate on the compressive strength of a glassy-bonded ceramic. The mechanisms causing the variation of compressive strength will be considered in this report.

The chemical reactions of the Silicon-Boron-Oxygen system are numerous and complex and have been investigated by Rizzo (Ref 10: 11-14). The results of the study of the kinetics of the chemical reactions in the Silicon-Boron-Oxygen system showed that the quantity of submicron precipitate could be controlled by the selection of the type of elemental boron used. The presence of the submicron precipitate is controlled by using amorphous boron instead of crystalline boron. Compositions investigated are 20 and 35 weight percent boron in the system.

The compressive strength of a ceramic material is not a unique value and generally follows a normal distribution curve. Si + 35% B is used as the model to determine the effects of the submicron precipitate. The composition of the boron is varied from 100% crystalline boron to 100% amorphous boron in increments of 25% amorphous boron. (i.e., 75% crystalline boron and 25% amorphous boron). A statistical evaluation is used for analyzing the experimental data. The student's t-distribution for small samples is applied to determine the 95% probability of a significant difference of the means between the various test compositions. The hypothesis that the means are equal is tested with the alternative hypothesis that the means are not equal. Ninety-five percent confidence limits are determined for compositions

exhibiting a significant difference of the means. The lower confidence limit is used to determine the percent of increase in the compressive strength due to the increasing amount of the submicron precipitate.

II. Literature Survey

A new type refractory was synthesized by sintering a mixture of elemental silicon and boron in air at 1400 °C. The sintered refractory is composed of unreacted silicon, SiB_4 , SiB_6 , and B_7O dispersed in a borosilicate matrix. The borosilicate matrix is distinguished by its stability at high temperatures and its resistance to attack by boiling water. Si, SiB_4 , SiB_6 , and B_7O phases act as the refractory components. The SiB_4 phase undergoes a peritectic decomposition into Si + SiB_6 above 1400 °C. This new refractory appears to be particularly attractive for use as a structural material in air at temperatures to 1550 °C. (Ref 11: 497-504). Some of the unusual properties of this new refractory are:

1. Oxidation resistant to boron oxide at temperatures as high as 1500°C in air.
2. Stable in boiling water.
3. Low electrical resistivity (1 to 100 ohm-cm).
4. Susceptor to high frequency field.
5. Low density (2.3 gm/cc).
6. Excellent thermal shock resistance.
7. High mechanical strength.
8. Easily fabricated.

A few of the physical and mechanical properties for this new refractory material have been determined by Isgrid (Ref 6:29).

1. Tensile strength, 10,200 psi at room temperature and 14,000 psi at 1300 °F.

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7. High mechanical strength.
8. Easily fabricated.

A few of the physical and mechanical properties for this new refractory material have been determined by Isgrid (Ref 6:29).

1. Tensile strength, 10,200 psi at room temperature and 14,000 psi at 1300 °F.

2. Compressive strength 64,000 to 89,100 psi.
3. Average Poisson's Ratio of 0.22
4. Modulus of elasticity of 36.2×10^6 psi at room temperature.
5. Modulus of elasticity in shear of 14.8×10^6 at room temperature.
6. Thermal Conductivity Coefficient of 31 BTU/(hr)(ft²)(°F/in) at 105 °F.
7. Average linear thermal expansion coefficient of 4.5 micro inches/in/°F from room temperature to 2000 °F.
8. Average specific heat of 0.188 BTU/lb - °F.

A typical microstructure after sintering a Si + 35 weight %B (crystalline) composition to 1400 °C in air is shown in Figure I.

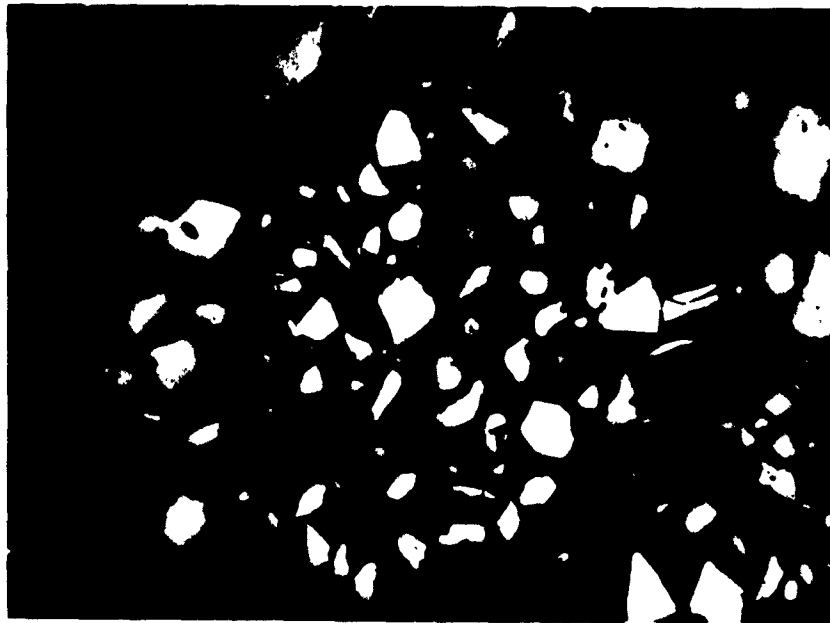
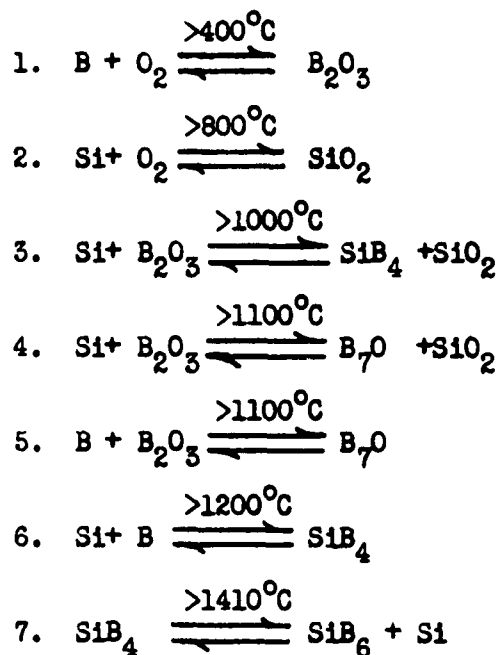


Figure I

The white phase is unreacted silicon; the grey phase is SiB₄, and the borosilicate matrix phase is black. The magnification is 480X and

the sample is unetched. Suboxide B_7O and SiB_6 can also exist as dispersed phases by knowledge of the kinetics of the reactions of the Si-B-O system. The kinetics of the reactions in the Si-B-O system were reported by Rizzo (Ref 10:15). The reactions responsible for the formation of this refractory by sintering Si + B mixtures to elevated temperatures in air are:



The presence of the dispersed phases (Si , SiB_4 , SiB_6 , B_7O , B) is controlled by the kinetics of these reactions and can provide a wide variety of desired microstructures. The suboxide B_7O is one of the hardest compounds (Vickers Hardness of 3900 Kgm/mm^2). The presence of B_7O can be controlled by using amorphous boron instead of crystalline boron. The suboxide, B_7O , reported by Rizzo, et. al., in this study of the oxidation of boron and silicon-boron compositions (Ref 10:12) has been tentatively identified as B_6O by Rizzo. (private communications).

A material may be considered to be in the brittle state when it exhibits a relatively small deformation before fracture. Ceramics are considered brittle state material and it has been found that brittle state materials do not exhibit a unique strength at which fracture occurs.

The design engineer is then faced with the problem of selecting a design stress at which the material has a known probability of fracture. The design stress of a brittle state material can be considered as that strength at which the material exhibits a tolerable probability of fracture. If a designer can tolerate no probability of fracture, the stress corresponding to zero probability of fracture must be determined experimentally. This means that a sufficient number of specimens must be evaluated in order that the data obtained may be treated by statistical techniques. Thus for each condition of application, a distribution curve of the properties of the material being considered must be determined. The designer must then use this distribution curve to select that design stress at which he can accept the corresponding probability of fracture. At first it would appear that considerable improvement in the distribution of strength values could be achieved by instituting good quality control methods. Unfortunately this does not seem to be the answer. This wide distribution of strength values has been found for many brittle materials. Theories by Griffith and Weibull which assume the presence of critical flaws in the structure appear to be verified by experimental results. Since it appears that flaws are an inherent property of brittle state materials

and that brittle state materials are flaw sensitive, then any design data concerning brittle state materials must be in the form of a distribution curve relating the strength property of interest to the probability of fracture at the corresponding strength level (Ref 1:10-11).

III. Experimental ProgramMaterials

The various grades of silicon and boron powders used as the raw materials in this investigation are listed in Table I.

Table I
Raw Materials

Material	Source	Grade	Particle Size	Manufacturer's Analysis (%)
Silicon	Union Carbide Corporation		-325 Mesh	99.81 Si 0.12 O 0.006 H 0.002 Fe
Boron*	U.S. Borax and Chemical Corp.	Crystalline	-325 Mesh	99.15 B 0.42 Mg 0.14 Al 0.13 Mn 0.05 Si
Boron*	U.S. Borax and Chemical Corp.	Amorphous	0.5 to 1.5 μ	95 to 97 B

* Grade of Boron used in this study will be designated by B_a (Amorphous) and B_c (Crystalline).

Composition Determination

Experimental compositions are indicated by weight percent of boron in the raw mixture. Composition limits used in this study are 20 and 35 weight percent boron, the remainder being silicon, and are based on previous information reported by Rizzo (Ref 11:500-501). Coalescence of the

silicon resulting in the "sweating out" of Si beads occurred in compositions of less than 10% boron. Compositions of more than 50% boron resulted in the formation of free boron oxide which hydrolyzes very readily, resulting in swelling and cracking of the refractory material.

The following four mixtures were prepared to determine the effects of the compressive strength of using amorphous or crystalline boron. The samples were prepared according to the procedure outlined in Chapter III (Sample Preparation, page 11).

1. Si + 20% B (amorphous)
2. Si + 20% B (crystalline)
3. Si + 35% B (amorphous)
4. Si + 35% B (crystalline)

Future reference to these four mixtures will be 20% B_a, 20% B_c, 35% B_a, and 35% B_c, respectively.

In order to determine the effect of the submicron precipitate, B₇O, on the compressive strength of the refractory material, the following intermediate mixtures were prepared:

1. Si + 35% B (25% of 35% B_a + 75% of 35% B_c)
2. Si + 35% B (50% of 35% B_a + 50% of 35% B_c)
3. Si + 35% B (75% of 35% B_a + 25% of 35% B_c)

Future references to these three mixtures will be 35% B_{ac} (25%,75%), 35% B_{ac} (50%,50%) and 35% B_{ac} (75%,25%) respectively.

Fabrication Techniques

The properties of ceramic bodies can be appreciably affected by

fabrication technique. Certain properties such as strength are to a degree dependent upon density; with maximum values approached as the bulk density approaches the theoretical density. The deviation of the bulk density from theoretical density may be used as a measure of the fabrication effectiveness (Ref 3: 367-368)

The common methods of fabricating ceramic bodies are slip casting, extruding, cold pressing (all followed by sintering), and hot pressing (performed at sintering temperature). A later fabricating method by vibratory compacting of ceramic powders has been investigated and results showed an increase of bulk densities over other low-temperature methods. (Ref 8: 2-14) The vibratory compacting techniques are only applicable to specimens of simple shapes.

Presintering of Raw Materials

Mixtures of 20% B_a, 20% B_c, 35% B_a, and 35% B_c were formed into pellets and sintered with a normal firing. (Ref Sintering Procedure, page 12). Weight gains of each composition are listed in Table V, Appendix B. The pellets were ground in a boron carbide mortar and passed through a 325 mesh screen. These compositions were then used as the raw materials in forming of the final cylindrical specimen.

Sample Preparation

Samples weighing 2.8 grams of the presintered compositions were formed by the vibratory compacting technique into cylindrical specimens. (0.95 cm diameter, length 2.5 cm) and then sintered by the normal firing schedule. The final sintered specimens were approximately 96 percent of

the reported theoretical density (2.3 gm/cc). Specific physical data on all machined specimens are listed in Table VI, Appendix B.

Sintering Procedure

Specimens were fired in a silicon carbide resistor furnace in a stagnant-air atmosphere. The normal firing schedule consisted of a heating rate of approximately 250 °C per hour with soaking periods of sixteen hours at 630 °C and one hour at peak temperature of 1410 °C.

Conversion of SiB_4 to SiB_6 was accomplished with a normal firing schedule except the peak temperature was raised to 1430 °C with a soaking period of three hours.

Machined Specimen Preparation

Sintered specimens were machined on a precision lathe using a "Crystolon" stone and approximately 0.1 cm of the diameter and 0.5 cm of the length were removed during the machining. The ends of the samples were then "lapped" on a leveling plate with 15 micron diamond grit and a vee block.

Compression Testing Procedure

The compressive load capacity was determined from machined specimens loaded perpendicular to the circular cross section. A Baldwin Universal Testing Machine (60,000 lbs capacity -- Serial No. F 45288) was used for the compressive tests. It was calibrated and had a maximum error of 0.40 percent over the range of 10,000 to 35,000 lbs. The ends of the test specimens were lubricated with powdered graphite and inserted in the

compression jig between Carboloy 78 B pads (Rockwell Hardness C 77), Figure 3, Appendix A. The assembled jig was placed between the platens of the testing machine and the load was applied at the rate of 3000 lbs per minute. The approximate platen speed for this constant loading rate was 0.008 inches per minute. Constant loading rate was maintained until the specimen fractured.

Analytical Procedures

Glass Analysis: Specimens from each test composition were ground to a fine powder in a boron carbide mortar. The powder was treated with 48% hydrofluoric acid until visible chemical reaction ceased and then heated to dryness. The hydrofluoric acid treatment removed the amorphous borosilicate glass from the specimen leaving the crystalline components. Weight losses from the acid treatment are tabulated in Table VII, Appendix B.

Relative Quantitative Analysis by X-Ray Diffraction Pattern: A General Electric XRD-3 X-Ray diffraction unit with Cu K α radiation was used to determine the phases present in the acid-treated specimens. A power setting of 46 KV and 16 Ma with a scanning rate of 2 degrees per minute was used. The 100 percent B $_7$ O peak ($2\theta = 34.9$ degrees) was used for relative quantitative determinations. All intensities were measured as the peak height above background radiation. Percentage increase of B $_7$ O was based on intensity of the B $_7$ O line of the 35% B $_c$ composition. (Ref 7: 410-438). Specific data of the quantitative determination is tabulated in Table VIII, Appendix B.

Metallographic Analysis: Samples of the test specimens were prepared by conventional techniques for microscopic examination. Polished surfaces were prepared with 240 grit grinding paper, 14 micron diamond grit, and No. 3 gamma alumina. Photomicrographs of all test compositions are taken at 480X magnification and enlarged by a factor of 1.84. Photomicrographs are included in Appendix A.

Statistical Analysis: Student's t distribution for small samples is used to determine the percent probability of a difference of the means between the composition containing an increasing percentage of amorphous boron and the composition containing 100% crystalline boron. The hypothesis that the means are equal was tested with the alternative hypothesis that they are not equal. Average breaking strength, \bar{X} , and variances, s^2 , are calculated for each series of compression tests of the same composition. Values of t are calculated for the compositions of increasing B_7O as compared to the composition containing 100 percent crystalline boron. Values of t greater than 95 percent probability indicated that there is a significant difference in the compressive strength of the materials. Ninety-five percent confidence limits are calculated for the compositions that indicated a significant difference in compressive strength (Ref 5: 211-242). A sample calculation and specific data are tabulated in Appendix C.

IV. Results and Discussion

Table II on page 16 presents the results of compressive tests on the four basic compositions (35% B_a, 35% B_c, 20% B_a, 20% B_c). Statistical evaluation is used to analyze the data in order to determine if there is a significant difference in the compressive strength of the refractory materials.

For illustration only, complete data and calculations are given for determining if there is a significant difference in the average compressive strength of 35% B_a and 35% B_c in Table IX and Table X, Appendix C. A significant difference with a probability of greater than 99% exists between the average compressive strengths. Ninety-five percent confidence limits for the difference of the means is used to calculate how large a difference is likely to exist. A minimum of 24,220 psi and a maximum of 52,780 psi can be expected to exist between the average compressive strength of 35% B_a and 35% B_c. This is a 95% probability of a 12.4 percent increase in the compressive strength of 35% B_c due to the submicron precipitate.

Similar calculations between 20% B_a and 20% B_c resulted in an acceptance of the hypothesis (t value = 0.260) that the means of the average compressive strength are equal. Statistically there is no increase in the mean strength of the two materials.

Intermediate compositions 35% B_a (25%, 75%), 35% B_{ac} (50%, 50%), 35% B_{ac} (75%, 25%) between 35% B_c and 35% B_a were fabricated to determine the effects of the submicron precipitate on the compressive strength.

Table II
Compressive Tests

Specimen No.	Composition	Load lbs.	X-Sectional Area in ²	Compressive Strength lbs/in ²
3 G	35% B _a	16,800	0.07645	219,700
4 G	35% B _a	17,200	0.07645	225,000
5 G	35% B _a	19,000	0.07645	248,500
6 G	35% B _a	18,075	0.07645	236,400
9 G	35% B _a	18,475	0.07645	241,600
26 F	35% B _c	15,275	0.07645	199,800
27 F	35% B _c	14,875	0.07645	194,600
29 F	35% B _c	14,175	0.07645	184,400
32 F	35% B _c	14,850	0.07645	194,200
6 L	35% B _c	15,650	0.07645	204,700
18 F	20% B _a	15,375	0.07645	201,100
19 F	20% B _a	14, 150	0.07645	185,100
20 F	20% B _a	16,175	0.07645	211,600
18 G	20% B _a	14,875	0.07645	194,600
28 G	20% B _a	17,650	0.07645	230,900
9 F	20% B _c	14,175	0.07645	185,400
13 F	20% B _c	15,300	0.07645	200,100
15 F	20% B _c	15,875	0.07645	207,600
23 G	20% B _c	16,500	0.07645	215,800
3 L	20% B _c	15,450	0.07645	202,100

Table III, page 18, presents the results of compressive tests on the three intermediate compositions.

A t-value of 0.239 (20% probability) resulted in the acceptance of the hypothesis that the means of the average compressive strengths of 35% B_{ac} (25%,75%) and 35% B_c are the same.

Comparison of 35% B_{ac} (50%,50%) and 35% B_c resulted in a t-value of 2.403 (probability of 96%) and an acceptance of the hypothesis that the average compressive strengths are significantly different. Determination of how large a real difference exists between the means is calculated to be a minimum of 547 psi and a maximum of 26,690 psi. This indicates that with any degree of certainty there is only about 547 psi increase in the average compressive strength. The result in terms of percent increase in strength is 0.3.

35% B_{ac} (75%,25%) and 35% B_c are compared and gave a t-value equal to 7.367 and a probability of greater than 99 percent, that there is a significant difference in their average compressive strength. This real difference is calculated to be a minimum of 20,540 psi and a maximum of 39,260 psi, and indicated that an increase of 10.5 percent in the average compressive strength of 35% B_c could be expected. Statistical data is presented for the five compositions in Table IV, page 19.

Specimens of 35% B_a and 35% B_c were heat treated at 1430 °C for three hours to convert SiB₄ to SiB₆. Coalescing and spheroidizing of the unreacted silicon considerably altered the microstructures when compared to the microstructures of the basic compositions of 35% B_a and 35% B_c. Results of compressive tests are presented in Table XI, Appendix C.

Table III
Compressive Tests

Specimen No.	Composition	Load lbs.	X-Sectional Area in ²	Compressive Strength lbs/in ²
17 K	35% B _{ac} (25%, 75%)	17,500	.0936	186,900
18 K	35% B _{ac} (25%, 75%)	18,075	.0923	195,800
19 K	35% B _{ac} (25%, 75%)	19,000	.0917	207,200
20 K	35% B _{ac} (25%, 75%)	18,100	.0939	192,800
23 K	35% B _{ac} (25%, 75%)	18,675	.0926	201,700
1 K	35% B _{ac} (50%, 50%)	16,050	.0767	209,300
3 K	35% B _{ac} (50%, 50%)	16,950	.0767	221,900
4 K	35% B _{ac} (50%, 50%)	15,450	.0767	201,400
6 K	35% B _{ac} (50%, 50%)	16,700	.0769	217,200
7 K	35% B _{ac} (50%, 50%)	15,150	.0769	197,000
11 K	35% B _{ac} (75%, 25%)	16,800	.0769	218,500
12 K	35% B _{ac} (75%, 25%)	17,000	.0767	221,600
13 K	35% B _{ac} (75%, 25%)	17,250	.0758	227,600
14 K	35% B _{ac} (75%, 25%)	17,750	.0764	232,300
15 K	35% B _{ac} (75%, 25%)	17,500	.0767	228,200

Table IV
Statistical Values of Basic Compositions

Composition	Average Compressive Strength (psi)	Variance $s^2 \times 10^{-6}$	Standard Deviation s	t-Value compared to 35% B _c	95% Confidence Limits for μ_{x-y} t=2.306		Minimum % Increase in Compressive Strength (psi)
					Minimum	Maximum	
35% B _c	195,740	41.5	6442				
35% B _{ac} (25%, 75%)	196,880	49.5	7036	.239			
35% B _{ac} (50%, 50%)	209,360	87.0	9327	2.403	547	26,690	0.3
35% B _{ac} (75%, 25%)	225,640	24.4	4940	7.367	20,540	39,260	10.5
35% B _a	234,240	111.8	10,574	6.218	24,220	52,780	12.4

Average compressive strengths of the converted compositions are not compared to the basic compositions because of the altered microstructures. Comparison of the average compressive strengths of the converted compositions gave a t-value of 2.873 (98% probability). The significant real difference of the averages is a minimum of 38,450 psi and a maximum of 71,020 psi.

Treatment of all the basic compositions with hydrofluoric acid to remove the borosilicate glass resulted in a weight decrease of approximately 70% (Table VII, Appendix B). The glass phase therefore remains approximately constant regardless of the starting composition and type of boron used. X-Ray diffraction patterns of the glass analysis residue provided data (Table VIII, Appendix B) to determine by quantitative X-Ray analysis the percent of increase in the submicron precipitate, B_7O . The intensity of the 100% B_7O peak ($2\theta = 34.9^\circ$) increased proportionally within 2.9% of the calculated value of the percent of B_7O present.

V. Summary and Conclusion

The compressive strength of the glass bonded ceramic is increased a minimum of 24,220 psi by the addition of a submicron precipitate, B_7O . The effect of the submicron precipitate on the compressive strength of the ceramic is negligible for less than a 50 percent increase. The major gain of 10.5% in the compressive strength occurred between 50 and 75 percent increase in the submicron precipitate and a minor gain of 1.9 percent is observed when the submicron precipitate was increased from 75 percent to 100 percent (Fig. 2, page 22).

The compressive strength of the 35% B_a ceramic is increased from a previously reported value of 89,100 psi (Ref 6:29) to 234,240 psi. This increase is due to improved fabrication techniques which eliminated visible surface cracks and increased the bulk densities.

Mechanical strengths of ceramic bodies are mainly dependent on internal stresses, surface condition, temperature, grain size, and porosity. (Ref 4: 24-33). The model ceramic used in this investigation is fabricated from the same elemental composition (silicon and boron). The variation is that of replacing crystalline boron with amorphous boron to introduce a submicron precipitate, B_7O . Variables that were held constant were grain size, surface condition, and temperature. Since the densities are equivalent, the effects of the porosity on the strength of 35% B_c and 35% B_a is considered negligible. Microstructures of the predominant crystalline components are considered equivalent except for the submicron precipitate, B_7O . The weight percent of borosilicate-glass

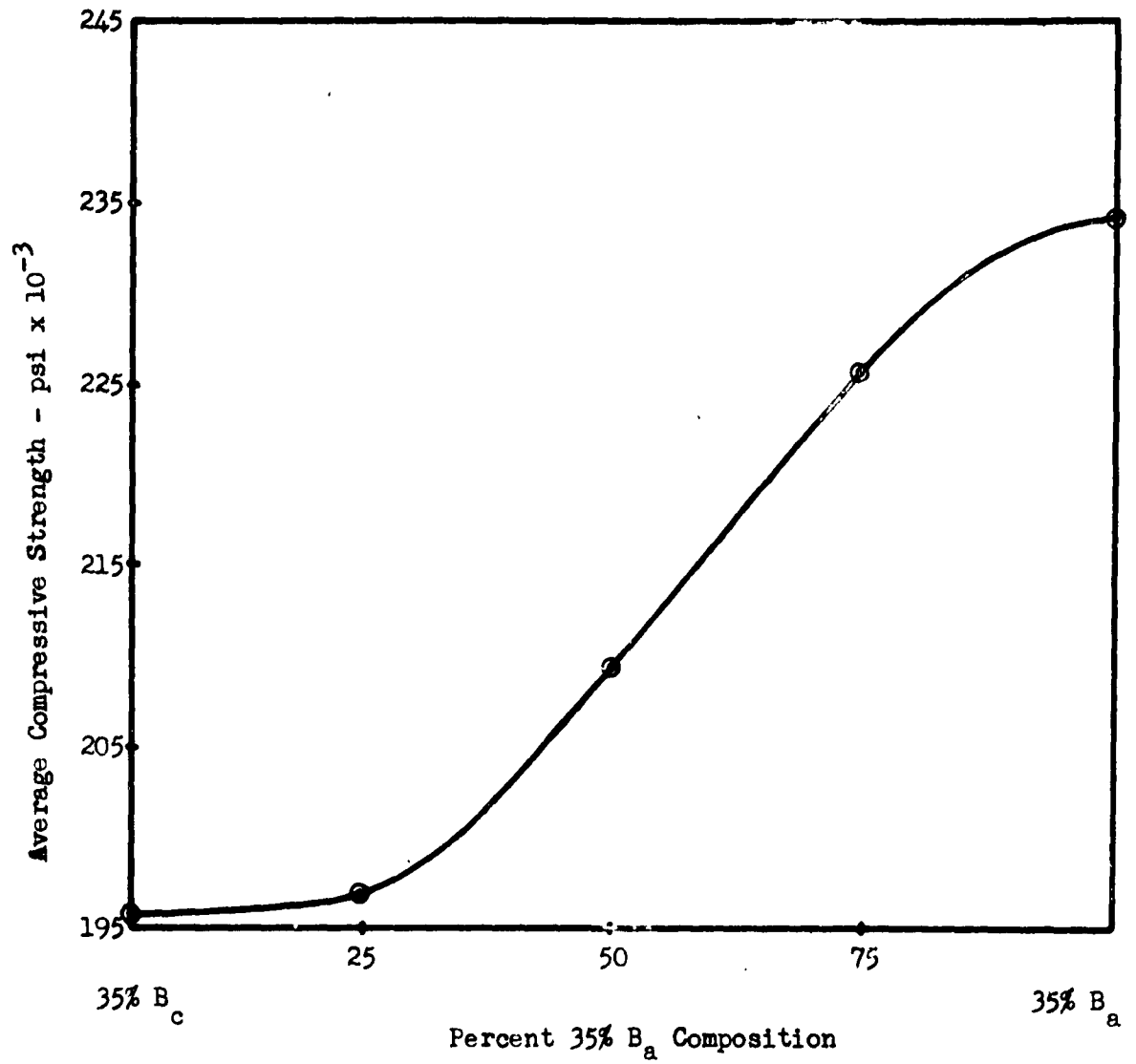


Figure 2
Compressive Strength vs. % Increase in 35% B_a

phase is approximately seventy percent for all compositions (Table VII, Appendix C).

A marked increase in internal stress has been observed by decreasing the grain size of the crystalline component of the ceramic. Internal stresses are also increased due to thermal expansion coefficient mismatch between the crystal and the glass phase present at the crystal boundary. The strength of the ceramic would depend on whether the induced internal stress is compatible with the load stress imposed on the fracturing medium. An increase in the strength of a material would imply that the internal stresses would oppose the load stresses. The load stress would therefore have to overcome the internal stresses before it could apply a stress to the fracturing medium (Ref 4: 32-36).

Griffith postulated the existence of microcracks in brittle material and the propagation of these microcracks will spread spontaneously if the decrease in strain energy is at least equal to the increase in surface energy. The strain energy is associated with the stress concentration at the crack ends. The cracks cannot propagate unless the energy is available from an external load. A crack propagation path would be impeded by a crystalline particle absorbing part of the strain energy. This would imply that additional external energy would be necessary to increase the strain energy for continued crack propagation. External energy would be available by increasing the external load on the specimen and the result would be an increase in strength of the material (Ref 4: 9-19).

The model used in this investigation is a highly stressed ceramic,

from observation of the condition of the specimen at failure (Fig. 3, Appendix A). Highly stressed glasses exhibit the same type of failure as the model ceramic. This analysis is based on simple internal stress configuration. The complexity of a polycrystalline ceramic body with regard to microstructure, composition, and a complex three-dimensional internal stress configuration has made the analysis of the factors affecting the mechanical properties extremely difficult. Thus, it is concluded that the increase in the compressive strength of 35% B compositions is due to the change of the internal stresses and impediment of crack propagation resulting from the introduction of the submicron precipitate, B_7O , into the borosilicate matrix.

VI. Recommendations

1. Determine the physical and mechanical properties of this high strength ceramic.
2. Study the effects of the fabrication technique on densities using a hydrostatic pressure cylinder.
3. Investigate the mechanisms responsible for the decrease in compressive strength due to the conversion of SiB_4 to SiB_6 .
4. Conduct chemical analysis on the borosilicate glass to determine its composition with various initial compositions.
5. Study the effects of elevated temperatures on the strength of the refractory material to determine its maximum useful temperature.
6. Conduct experiments by employing silicon particles of various sizes to study their effects on the compressive strength.

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Appendix A

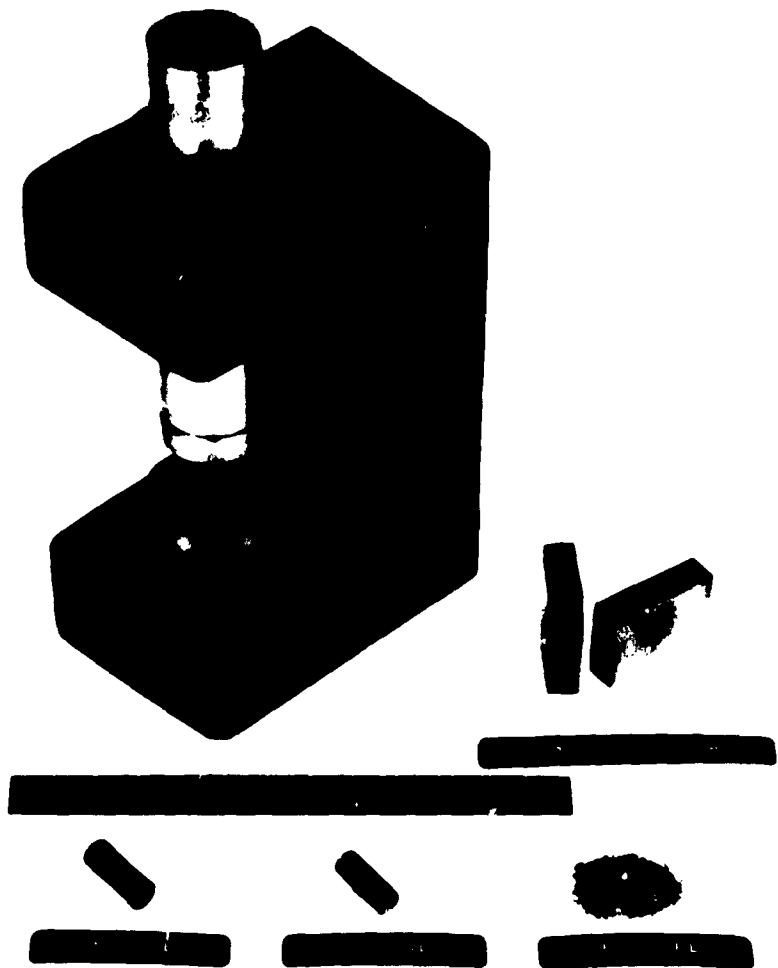


Figure 3
Compressive Test Jig

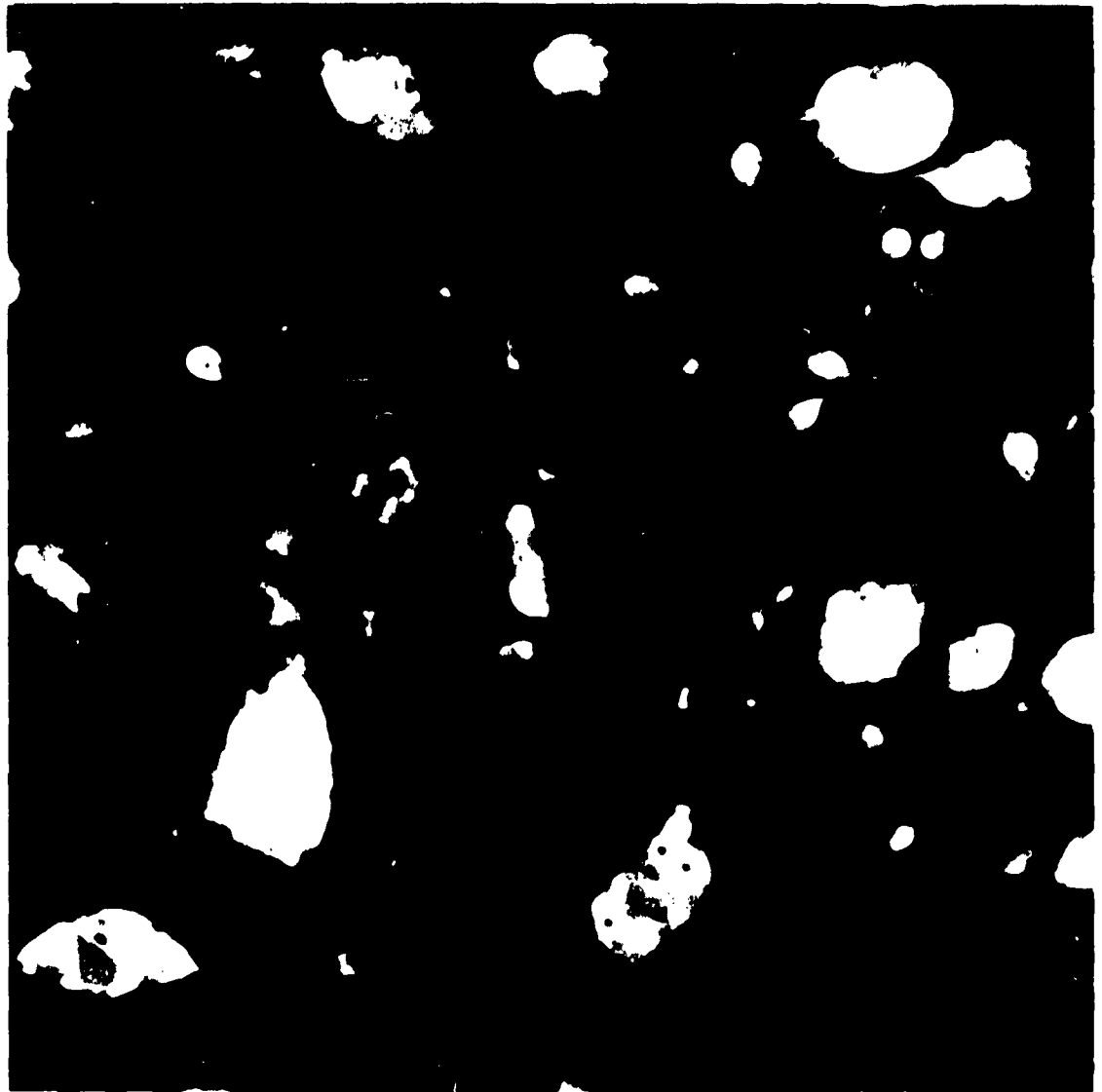


Figure 4

Photomicrograph of a Si + 35% B₂O₃ after heating at 630 °C for 16 hours followed by heating at 1410 °C for 1 hour in air. The white phase is Si, the gray phase surrounding the Si particles is SiB₄, and the sub-micron precipitate in the borosilicate matrix is B₂O₃. Magnification 480X, unetched.

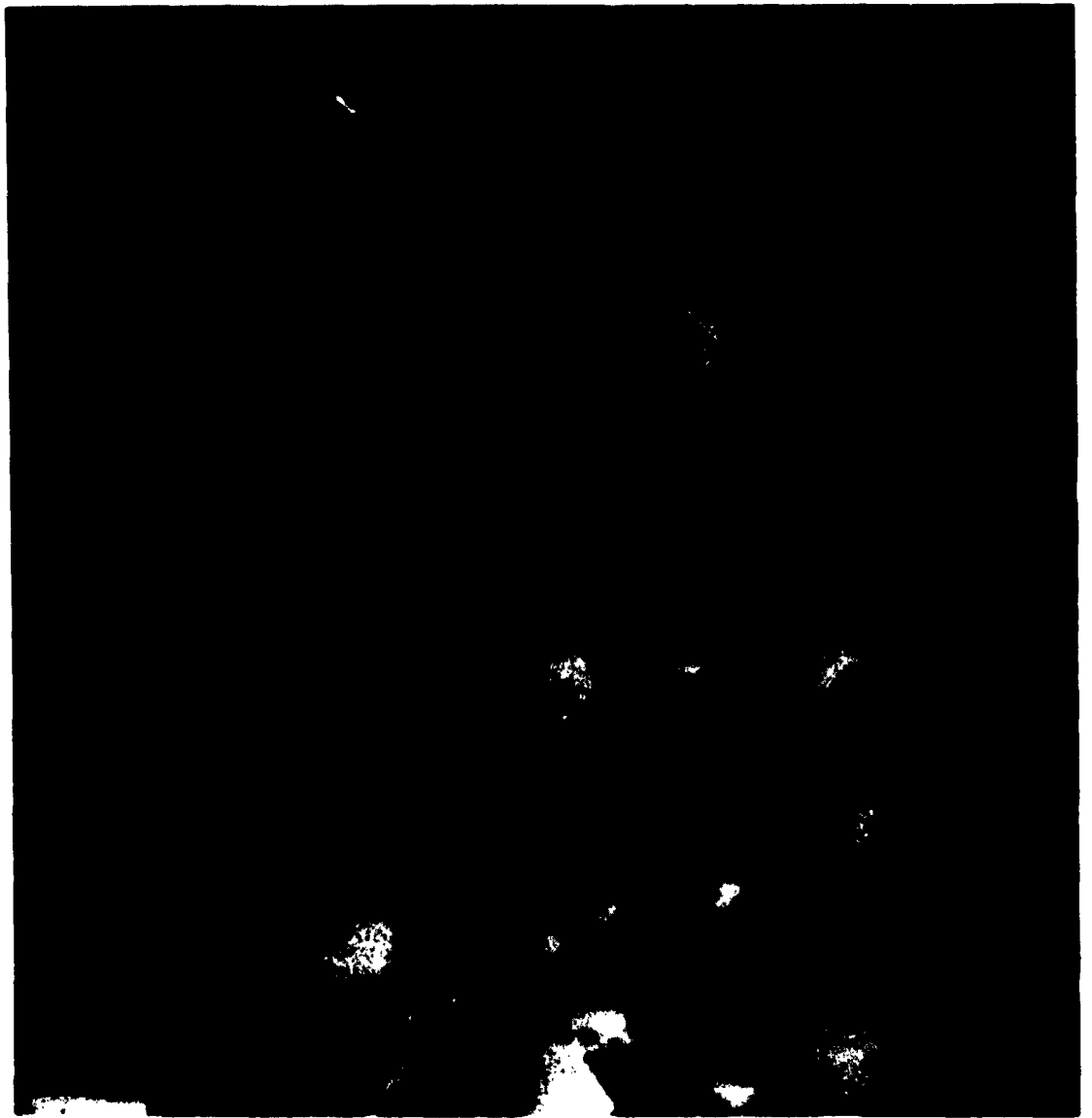


Figure 5

Micrograph of a Si + 35% B alloy after heating at 1030 °C for 16 hours followed by heating at 1410 °C for 1 hour in air. The white phase is Si, the phase surrounding the Si particles is SiB₄, and the black phase is boron-rich matrix. Magnification 480X, unetched.

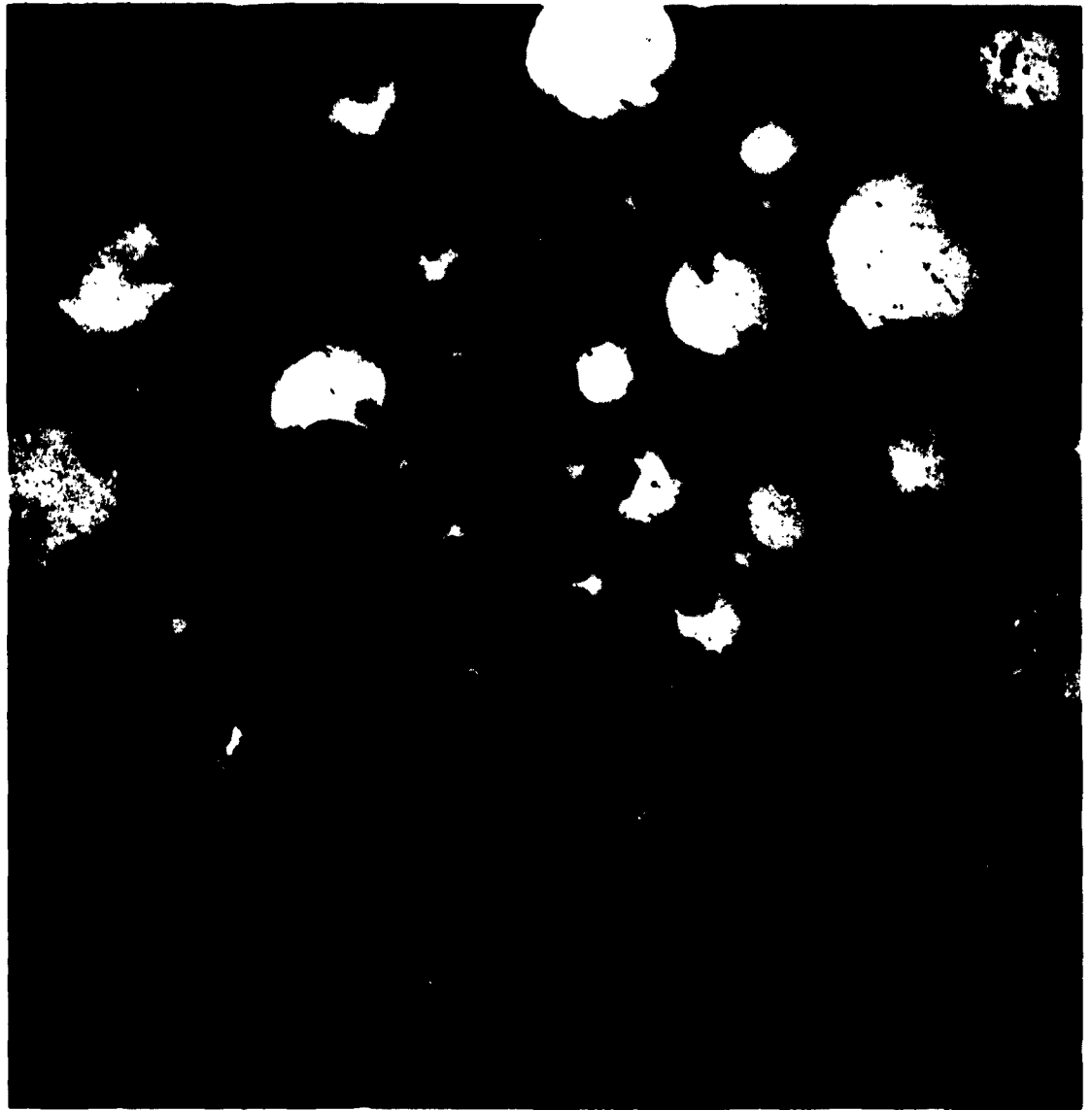


Figure 6

Photomicrograph of a $\text{Si} + 20\% \text{B}_2\text{O}_3$ after heating at 630°C for 16 hours followed by heating at 1410°C for 1 hour in air. The white phase is Si , the gray phase surrounding the Si particles is SiB_4 , and the sub-micron precipitate in the borosilicate matrix is B_2O_3 . Magnification 480X, unetched.



Figure 7

Photomicrograph of a $\text{Si} + 20\% \text{B}$ after heating at 630°C for 16 hours followed by heating at 1410°C for 1 hour in air. The white phase is Si , the grey phase surrounding the Si particles is SiB_2 , and the black phase is the borosilicate matrix. Magnification $480\times$; unetched.



Figure 8

Photomicrograph of a Si + 35% B_{ac} (25%, 75%) after heating at 630° C for 16 hours followed by heating at 1410 °C for 1 hour in air. The white phase is Si, the gray phase surrounding the Si particles is SiB₄, and the submicron precipitate in the borosilicate matrix is B₇O. Magnification 480X, unetched.

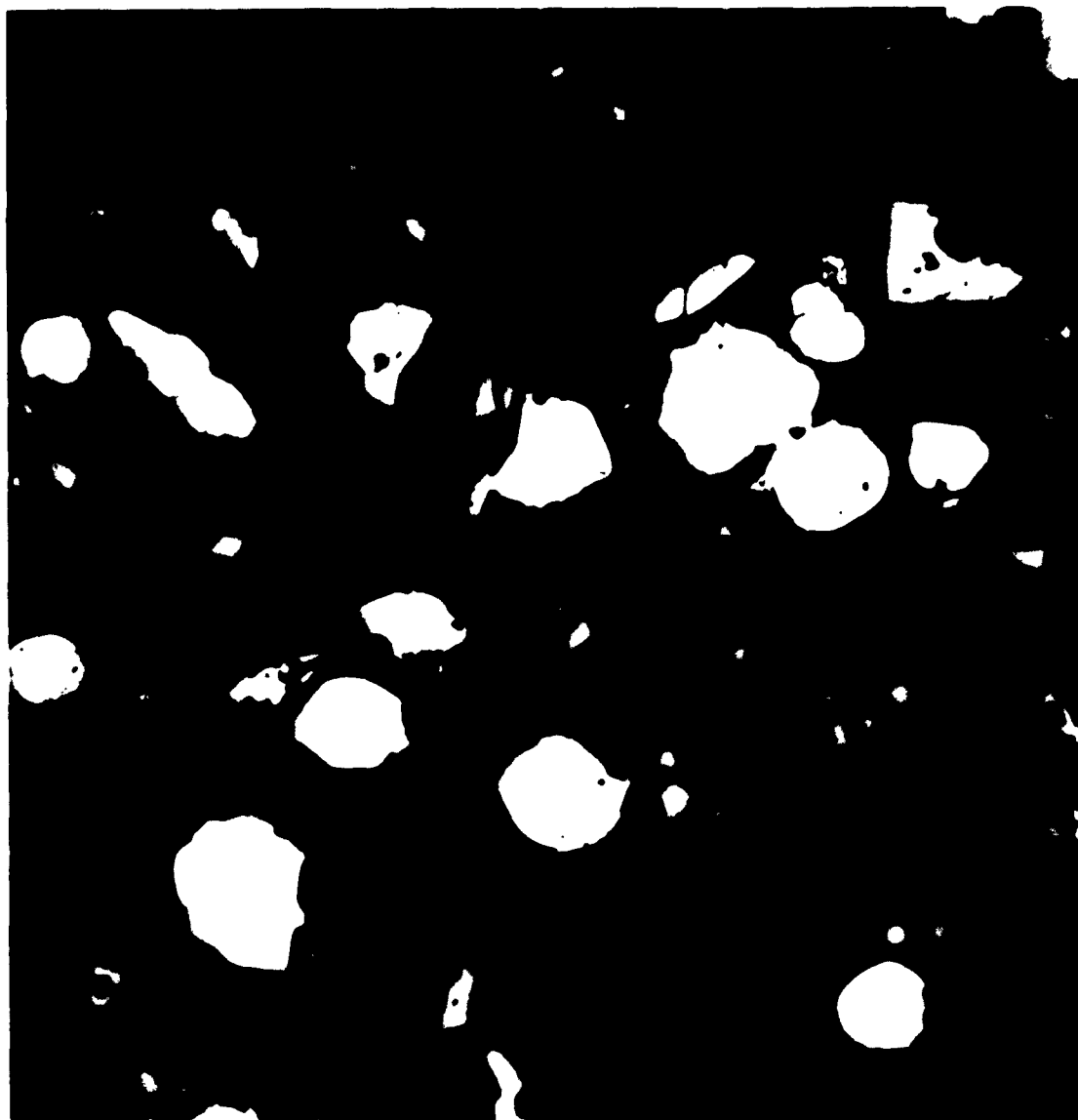


Figure 9

Photomicrograph of a Si + 35% B₂O₃ (50%, 50%) after heating at 630 °C for 16 hours followed by heating^{ac} at 1410 °C for 1 hour in air. The white phase is Si, the grey phase surrounding the Si particles is SiB₃, and the submicron precipitate in the borosilicate matrix is B₇O. Mag⁴nification 480X, unetched.



Figure 10

Photomicrograph of a Si + 35% B₂O₃ (75%, 25%) after heating at 630 °C for 10 hours followed by heating^{ac} at 1410 °C for 1 hour in air. The white phase is Si, the gray phase surrounding the Si particles is SiB₃, and the submicron precipitate in the borosilicate matrix is B₇O₃. Magnification 480X, unetched.

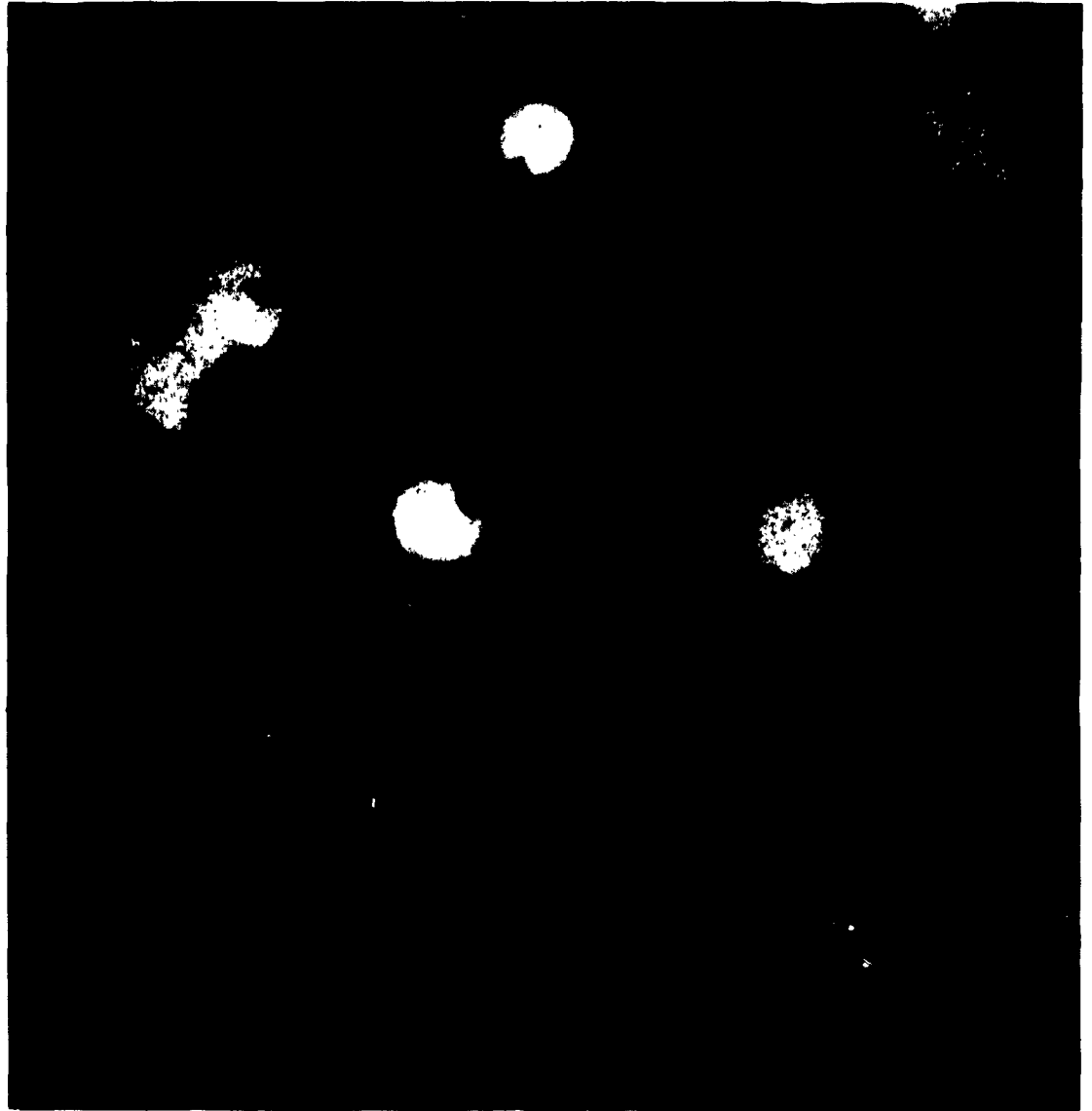


Figure 11

Photomicrograph of a Si + 35% B₇O₆ after heating at 630 °C for 16 hours followed by heating at 1430 °C for 3 hours in air. The white phase is Si, the grey phase surrounding the Si particles is SiB₆, and the sub-micron precipitate in the borosilicate matrix is B₇O₆. Magnification 480X, unetched.



Figure 12

Photomicrograph of a Si + 35% B₂O₃ after heating at 1300°C for 1 hour followed by heating at 1430°C for 3 hours in air. The white phase is Si, the gray phase surrounding the Si particles is SiO₂, and the black phase is the borosilicate matrix. Magnification 13X, and 1000X.

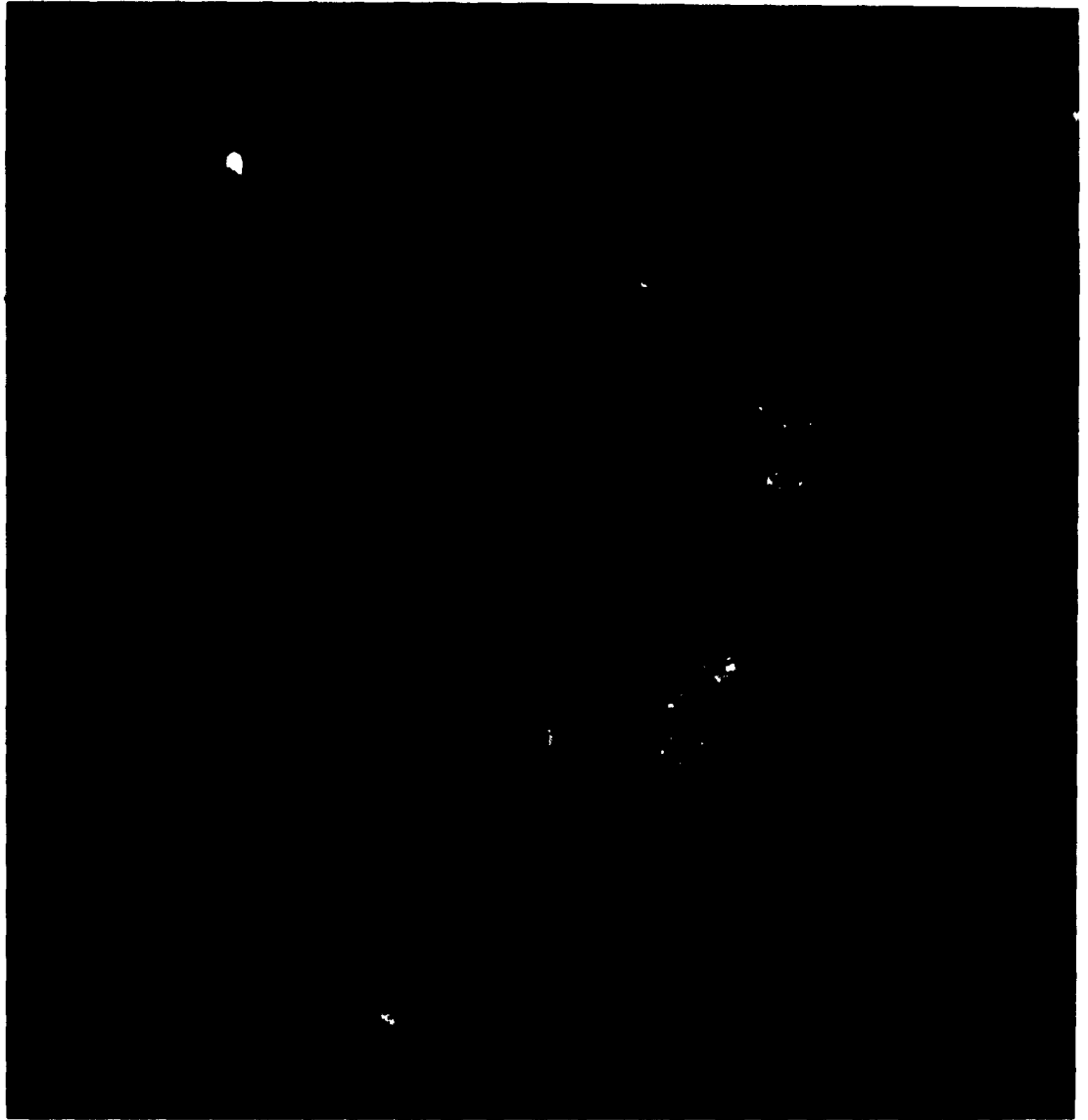


Figure 13

Photomicrograph of a $\text{Si} + 20\% \text{B}_2\text{O}_3$ after heating at 630°C for 16 hours followed by heating at 1430°C for 3 hours in air. The white phase is Si, the grey phase surrounding the Si particles is SiB_3 , and the sub-micron precipitate in the borosilicate matrix is B_2O_3 . Magnification 480X, unetched

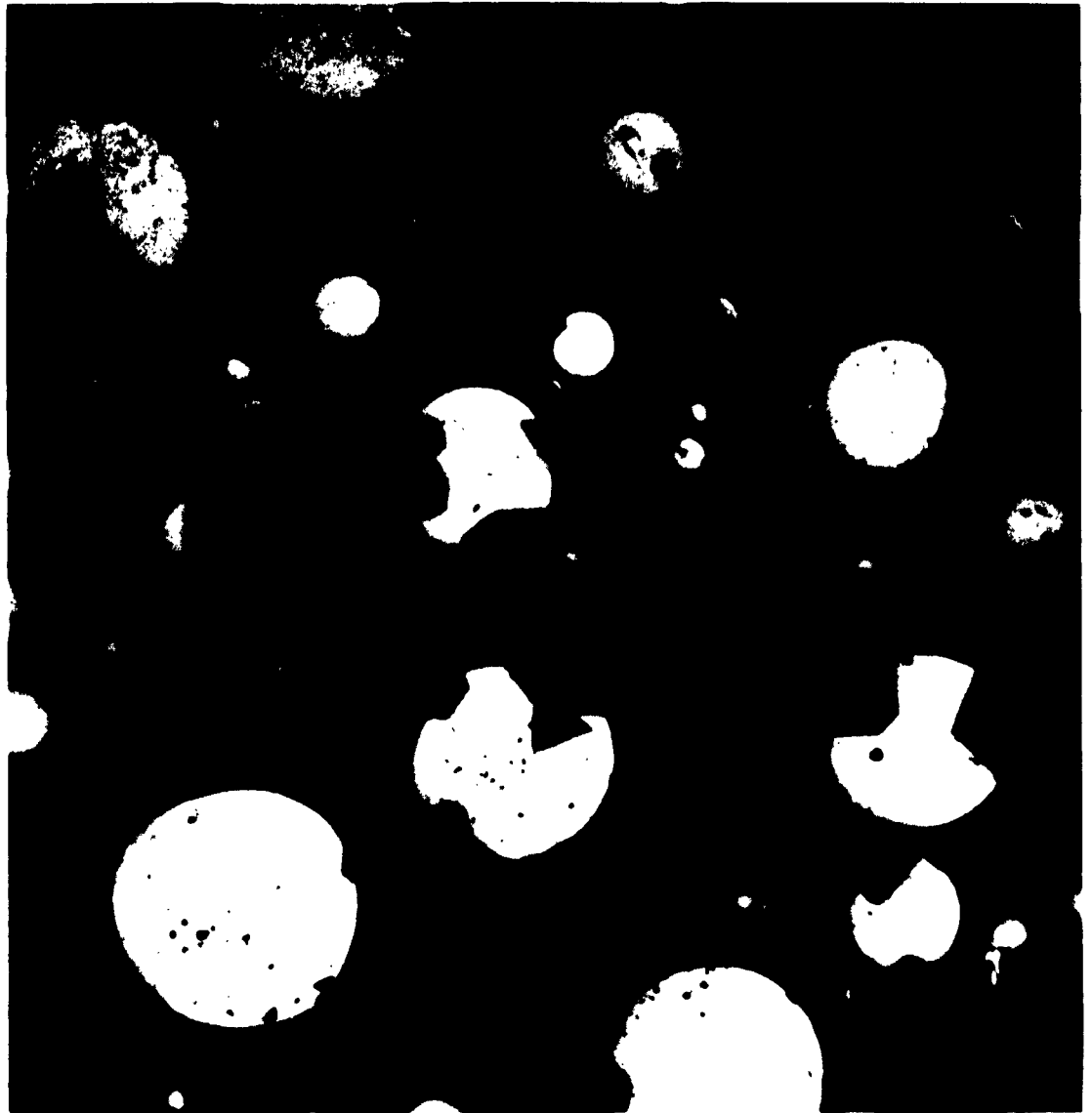


Figure 14

Photomicrograph of a Si + 20% B after heating at 630 °C for 16 hours followed by heating at 1430 °C for 3 hours in air. The white phase is Si, the gray phase surrounding the Si particles is SiB₃, and the black phase is the borosilicate matrix. Magnification 480X,⁶ unetched.

Appendix B

Table V

Percent Weight Gains of Compositions

Composition	Percent of Weight Gain	
	1st. Firing	2nd. Firing
20% B _a	34.5	10.5
20% B _c	27.3	17.1
35% B _a	37.2	10.5
35% B _c	28.8	16.5
35% B _{ac} (25%, 75%)	30.9	9.9
35% B _{ac} (50%, 50%)	33.0	12.3
35% B _{ac} (75%, 25%)	35.1	9.7

Table VI
Machined Specimens

Specimen No.	Composition	Weight (gm)	Diameter (cm)	Length (cm)	Bulk Density (gm/cc)
3 G	35% B _a	2.445	.79248	2.2225	2.230
4 G	35% B _a	2.441	.79248	2.2225	2.227
5 G	35% B _a	2.424	.79248	2.2225	2.211
6 G	35% B _a	2.415	.79248	2.2225	2.228
9 G	35% B _a	2.449	.79248	2.2225	2.234
26 F	35% B _c	2.417	.79248	2.2225	2.205
27 F	35% B _c	2.379	.79248	2.2225	2.170
29 F	35% B _c	2.408	.79248	2.2225	2.196
32 F	35% B _c	2.430	.79248	2.2225	2.217
6 L	35% B _c	2.448	.79248	2.2225	2.233
18 F	20% B _a	2.312	.79248	2.1082	2.223
19 F	20% B _a	2.301	.79248	2.1082	2.213
20 F	20% B _a	2.297	.79248	2.1082	2.209
18 G	20% B _a	2.331	.79248	2.1082	2.242
28 G	20% B _a	2.324	.79248	2.1082	2.235

Table VI (continued)

Specimen No.	Composition	Weight (gm)	Diameter (cm)	Length (cm)	Bulk Density (gm/cc)
9 F	20% B _c	2.229	.79248	2.1082	2.218
13 F	20% B _c	2.226	.79248	2.1082	2.215
15 F	20% B _c	2.225	.79248	2.1082	2.214
23 G	20% B _c	2.259	.79248	2.1082	2.228
3 L	20% B _c	2.218	.79248	2.1082	2.207
17 K	35% B _{ac} (25%, 75%)	2.795	0.877	2.107	2.196
18 K	35% B _{ac} (25%, 75%)	2.609	0.871	1.967	2.226
19 K	35% B _{ac} (25%, 75%)	2.633	0.868	2.012	2.212
20 K	35% B _{ac} (25%, 75%)	2.815	0.878	2.098	2.216
23 K	35% B _{ac} (25%, 75%)	2.270	0.872	2.092	2.217
1 K	35% B _{ac} (50%, 50%)	2.463	0.794	2.267	2.194
3 K	35% B _{ac} (50%, 50%)	2.369	0.792	2.174	2.212
4 K	35% B _{ac} (50%, 50%)	2.331	0.794	2.136	2.204
6 K	35% B _{ac} (50%, 50%)	2.305	0.795	2.096	2.215
7 K	35% B _{ac} (50%, 50%)	2.411	0.795	2.223	2.185

Table VI (continued)

Specimen No.	Composition	Weight (gm)	Diameter (cm)	Length (cm)	Bulk Density (gm/cc)
11 K	35% B _{ac} (75%, 25%)	2.260	0.795	2.054	2.217
12 K	35% B _{ac} (75%, 25%)	2.211	0.794	2.014	2.217
13 K	35% B _{ac} (75%, 25%)	2.189	0.789	2.007	2.231
14 K	35% B _{ac} (75%, 25%)	2.282	0.792	2.098	2.208
15 K	35% B _{ac} (75%, 25%)	2.321	0.794	2.117	2.215
2 J	35% B _a (S1B ₆)	2.565	0.819	2.177	2.237
3 J	35% B _a (S1B ₆)	2.198	0.749	2.242	2.225
4 J	35% B _a (S1B ₆)	2.325	0.783	2.163	2.232
6 J	35% B _a (S1B ₆)	2.521	0.806	2.217	2.229
7 J	35% B _a (S1B ₆)	2.509	0.814	2.157	2.235
10 J	35% B _c (S1B ₆)	2.559	0.831	2.147	2.198
11 J	35% B _c (S1B ₆)	2.470	0.826	2.099	2.196
13 J	35% B _c (S1B ₆)	2.620	0.833	2.171	2.214
3 E	35% B _c (S1B ₆)	2.675	0.844	2.159	2.215
7 E	35% B _c (S1B ₆)	2.765	0.830	2.290	2.231

Table VII
Glass Phase Analysis (Wgt %)

Specimen No.	Composition	Specimen Weight (gm)	Weight after HF Treatment (gm)	Weight Loss (gm)	% Glass Phase
5 G	35% B _a	2.307	0.714	1.657	70.8
27 F	35% B _c	1.903	0.596	1.298	68.2
28 G	20% B _a	2.245	0.715	1.575	70.0
9 F	20% B _c	2.150	0.676	1.461	67.8
23 K	35% B _{ac} (25%, 75%)	2.612	0.876	1.736	66.5
1 K	35% B _{ac} (50%, 50%)	2.109	0.620	1.489	70.6
15 K	35% B _{ac} (75%, 25%)	2.005	0.621	1.384	69.5
2 J	35% B _a (SiB ₆)	2.065	0.650	1.415	68.6
3 E	35% B _c (SiB ₆)	2.324	0.751	1.573	67.7

Table VIII

Quantitative X-Ray Analysis for B_7O Content

Note: 100% B_7O peak ($2\theta = 54.9$ degrees) was used for analysis.

Specimen No.	Composition	Peak Intensity (inches)	Relative % Increase in B_7O	
			X-Ray Analysis	Calculated
3 G	35% B_a	5.48	100.0	100
15 K	35% B_{ac} (75%, 25%)	4.28	72.1	75
1 K	35% B_{ac} (50%, 50%)	3.35	48.2	50
23 K	35% B_{ac} (25%, 75%)	2.25	24.9	25
27 K	35% B_c	1.18	0	0

Appendix C

Sample Calculation

Table IX Compressive Test Data

Specimen No.	Composition	Load (lbs)	X-Sectional Area (in ²)	Compressive Strength (lbs/in ²)
3 G	35% B _a	16,800	0.07645	219,700
4 G	35% B _a	17,200	0.07645	225,000
5 G	35% B _a	19,000	0.07645	248,500
6 G	35% B _a	18,075	0.07645	236,400
9 G	35% B _a	18,475	0.07645	241,600
26 F	35% B _c	15,275	0.07645	199,800
27 F	35% B _c	14,875	0.07645	194,600
29 F	35% B _c	14,175	0.07645	184,400
32 F	35% B _c	14,850	0.07645	194,200
6 L	35% B _c	15,650	0.07645	204,700

Table X

Statistical Calculations for 35% B_a and 35% B_c

Computation	35% B _a	35% B _c
Average = $\bar{x} = \frac{\text{Total}}{\text{No Values}}$	234,240	195,740
N = no of Specimens	5	5
$\frac{\sum x_i^2}{N} = \frac{x_1^2 + x_2^2 + \dots + x_n^2}{N}$	5.49802×10^{10}	3.83556×10^{10}
\bar{x}^2	5.48684×10^{10}	3.83141×10^{10}
$s^2 = \frac{\sum x_i^2}{N} - \bar{x}^2$	111.8×10^6	41.5×10^6
Standard Deviations = S	± 10574	± 6442

Student's t - test

Testing hypothesis of the population means, H₀: $\mu_x = \mu_y$ Against the alternative H₁: $\mu_x > \mu_y$

$$t = (\bar{x} - \bar{y}) - (\mu_x - \mu_y) \left[\frac{N_x + N_y - 2}{2(s_x^2 + s_y^2)} \right]^{\frac{1}{2}}$$

$$t = (234,240 - 195,740) \left[\frac{5 + 5 - 2}{2(111.8 \times 10^6 + 41.5 \times 10^6)} \right]^{\frac{1}{2}}$$

$$t = 6.218$$

For 95% Probability, the value of $t = 2.306$

Therefore there is a significant difference between the population means of 35% B_a and 35% B_c.

Value of difference of the means with 95% confidence limits

$$\begin{aligned}
 (\mu_x - \mu_y) &= (\bar{x} - \bar{y}) \pm t \left[\frac{2(s_x^2 + s_y^2)}{N_x + N_y - 2} \right]^{\frac{1}{2}} \\
 &= (234,240 - 195,740) \pm 2.306 \left[\frac{2(111.8 \times 10^6 + 41.5 \times 10^6)}{5 + 5 - 2} \right]^{\frac{1}{2}} \\
 &= 38,500 \pm 14,280 \\
 24,220 &< \mu_x - \mu_y < 52,780
 \end{aligned}$$

From this result, one can expect with 95% probability, that the minimum difference between the compressive strength means will be 24,220 lbs/in².

The percent increase in compressive strength from 35% B_c to 35% B_a due to the submicron precipitate would be:

$$\frac{24,220 \times 100}{195,740} = 12.4\% \text{ (minimum)}$$

$$\frac{52,780 \times 100}{195,740} = 27.2\% \text{ (maximum)}$$

Table XI
Compression Tests

Specimen No.	Composition	Load (lbs)	X-Sectional Area (in ²)	Compressive Strength (lbs/in ²)
2 J	35% B _a (S1B ₆)	19,500	.0817	238,700
3 J	35% B _a (S1B ₆)	14,200	.0685	207,900
4 J	35% B _a (S1B ₆)	15,400	.0746	206,400
6 J	35% B _a (S1B ₆)	18,000	.0791	227,600
7 J	35% B _a (S1B ₆)	16,500	.0807	204,500
10 J	35% B _c (S1B ₆)	13,650	.0841	162,300
11 J	35% B _c (S1B ₆)	13,175	.0831	158,500
13 J	35% B _c (S1B ₆)	13,675	.0845	161,800
3 E	35% B _c (S1B ₆)	14,650	.0867	169,000
7 E	35% B _c (S1B ₆)	13,400	.0859	159,700